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Modeling for the optimal biodegradation of toxic wastewater in a discontinuous reactor

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Abstract The degradation of toxic compounds poses inhibition problems when treated in Sequencing Batch Reactors (SBR). Time Optimal Control (TOC) methods may be used to avoid such inhibition and to exploit the maximum capabilities of this class of reactors. However, a good understanding, i.e. modeling, of the SBR is needed in order to implement TOC methods. Biomass and substrate online measurements are usually unavailable for wastewater applications, so TOC must use only related variables as dissolved oxygen and volume. Although the standard mathematical model to describe the reaction phase of such SBRs is good enough for explaining its general behavior in uncontrolled batch mode, better detail is needed to model its dynamics when the reactor operates near the maximum degradation rate zone, as when TOC is used. In this paper two improvements to the model are suggested: to include the sensor delay effects and to modify the classical Haldane curve in a piecewise manner. These modifications offer a good solution for a reasonable complexification tradeoff. Additionally a new way to look at the Haldane K-parameters (μ_o, K_I, K_S) is described, the S-parameters (μ^*, S^*, S_m). These parameters do have a clear physical meaning, independent of each other and, unlike the K-parameters, allow statistical treatment to find a single model for multiple experiments data.
Keywords Haldane model; inhibition; mathematical model; SBR; time optimal control; 4-chlorophenol

Introduction

The industrial wastewaters containing toxic compounds generated by several chemical and petrochemical facilities often cause operational problems in continuous flow systems. The discontinuous processes (controlled unsteady state processes) have been explored in order to increase the biotreatment efficiencies of wastewater (Wilderer *et al.*, 2001). These processes, also called Sequencing Batch Reactors (SBR), are flexible in the control operation and can be automated. The SBR operates under five phases: fill, react, settle, draw, and idle. The way in which the duration of each one of these phases is determined can be denominated operation mode and has a fundamental impact in the SBR characteristics. Despite the inherent advantages of the discontinuous processes in relation to the biodegradation of toxic substances, the SBR operated under the conventional operation modes present several constraints when they are applied to the toxic wastewater degradation: inhibition of the microorganisms, problems with shock loads of toxic compounds, deacclimation and problems of starvation of the microorganisms and low efficiencies regarding the removal of toxic compounds (Buitrón and Moreno 2004; Buitrón *et al*, 2003). To avoid such problems and to exploit the maximum capabilities of the discontinuous reactors, Time Optimal Control (TOC) strategies can be applied (Betancur *et al*., 2004). However, a good understanding, i.e. modeling, of the SBR is needed in order to implement the TOC methods. The standard mathematical model used to describe the reaction phase in the SBR is good enough for explaining the general behavior in uncontrolled batch mode. On the other hand, better detail is needed to model its dynamics when the reactor operates near the maximum degradation rate zone. This is the case when an optimal control strategy is applied. In order to directly apply TOC strategies, substrate measurements might be necessary. But, in practice biomass and substrate online measurements are usually unavailable. To overcome this constraint it has been proposed the estimation of the substrate and biomass concentrations from the on line measurement of the dissolved oxygen (DO) (Vargas *et al*., 2000).

The objective of the paper is to develop and validate an improved mathematical model for the filling and reaction phases of a discontinuous reactor. The findings are applied to explain the Sequencing Batch Reactor (SBR) behavior when a Time Optimal Control (TOC) law is applied, i.e. when the reactor is kept around its maximum degradation rate point most of the time.

Methodology

An aerobic automated Sequencing Batch Reactor (SBR) system with a capacity of 7L and an exchange volume of 57% was used (Figure 1). The airflow rate was 1.5 liters per minute and the temperature was maintained at 20 ºC inside the reactor. The reactor was inoculated with microorganisms coming from a municipal activated sludge treatment plant (2000 mgVSS/L). A synthetic wastewater containing 4-chorophenol (4CP) as a model of the toxic compounds was used as a sole source of carbon and energy. The reactor was acclimated to properly operate when an influent concentration of 350 mg 4CP/L was used in Fixed Time Control (FTC) batch mode. Nutrients such as nitrogen, phosphorus, and oligoelements were added following the techniques recommended by ANFOR (1985). The SBR was operated under the following strategy: preaeration time (15 min), filling and reaction time (variable depending on the necessary time to reach a removal efficiency of 4CP of 99%), settling time (30 min) and draw time (6 min).

Dissolved Oxygen (DO) concentration was measured online using a COS4 Endress+Hauser sensor. The substrate concentration was measured taking samples and processing them offline using the colorimetric technique of the 4-aminoantipyrine method (Standard Methods, 1992). Total and volatile suspended solids (TSS and VSS) analyses were determined according to the Standard Methods (1992). Dissolved organic carbon was determined with a Shimadzu TOC-5050 and chemical oxygen demand according to Standard Methods (1992). Theses analyses were performed to evaluate the 4CP mineralization.

Initially experiments where done in FTC batch mode. DO and 4CP data were obtained and used to identify the model parameters in its classical form and compare the simulation results with the observed behavior. A modification to the model was introduced and the same process for identifying the parameters was followed and simulation results compared to experimental data. Finally, simulations were done to compare model predictions to real data using a TOC strategy.

Figure 1 Pilot reactor utilized for the toxic compounds degradation

Results and discussion

Modeling

For finding a mathematical model that represents the reaction phase behavior of the SBR two general principles were followed: to keep the model simple, while adequately representing the desired behavior, and to separate, when possible, the identification of the yield (static) parameters from the identification of the kinetic (dynamic) parameters. Various methods for yield parameter identification were tested. The best results were obtained using direct measures from biomass growth and substrate consumption after a succession of reactions. Kinetic parameters were identified using MATLAB's "lsqnonlin" tool. The classical model used is represented in space-state form by equation (1):

$$\begin{aligned}
\frac{dX}{dt} &= \mu X - X\,\frac{q_{in}}{V} \\
\frac{dS_C}{dt} &= -k_1 \mu X + \left(S_{C,in} - S_C\right)\frac{q_{in}}{V} \\
\frac{dS_O}{dt} &= -k_2 \mu X - bX + K_L a * \left(S_{Os} - S_O\right) + \left(S_{O,in} - S_O\right)\frac{q_{in}}{V} \\
\frac{dV}{dt} &= q_{in}
\end{aligned} \qquad \text{Eq.(1)}$$

Where: X, Sc, So, $Sc_{,in}$, $So_{,in}$, So_s, V, q_{in}, μ, K_La, b, k_1 and k_2 represent the biomass, toxic substrate, DO in the reactor, inlet toxic substrate, inlet DO and DO saturation concentrations, volume level, the inlet flow rate, the specific growth rate, the oxygen transfer coefficient, the endogenous respiration kinetic constant and the yield coefficients, respectively.

A set of different kinetics experiments was conducted. Each experiment was identified separately, i.e. a set of parameters was found, the one that better explained the individual results for a given fitting criteria. The chosen criteria weighted both DO and Substrate errors. After individual models were available, a single model was chosen by extracting the mean value of each parameter. Confidence intervals were calculated in order to asses the confidence of the mean model. Then infinite time horizon model simulations were compared to actual data.

After analyzing the SBR behavior it is clear that a close relation between DO consumption and maximum microorganism activity exists. In batch mode, two minimum DO peaks are clearly visible for each batch, one early when filling the reactor and the other when the reaction is almost finishing (Figure 2). It was observed that the substrate kinetics match acceptably, i.e. inside the expected experimental measurement error, while DO did not, at least not in the zone of interest, i.e. while the minimum DO peaks do happen. After various exploratory explanations (Moreno *et al*. 2003) it was decided to add two additional state variables to the model, in order to include the effects of DO sensor delay. This was done because in all collected data, when compared to the model simulation, actual DO exhibited a delay in its response to get into the minimum peaks or to exit from them. As no biological reasons were suspected for this behavior the DO sensor was the remaining suspect. A step response test was done to the DO sensor and a second order model was obtained to explain it. Result showed that time constants of the DO sensor are faster than those of the biological system, but are not fast enough to be ignored when the system transits near the maximum value of the Haldane curve, i.e. when DO minimum peaks are to be expected. Equation (2) describes the DO sensor's dynamics:

$$\begin{aligned}
\frac{dS_{Oa}}{dt} &= (S_O - S_{Oa})/\tau_a \\
\frac{dS_{Osen}}{dt} &= (S_{Osen} - S_{Oa})/\tau_b
\end{aligned} \qquad \text{Eq.(2)}$$

Where: So, So_{sen}, So_a, τ_a and τ_b represent the actual DO concentration, sensed (measured) DO concentration, auxiliary intermediate DO concentration, and the sensor's time constants, respectively.

Another difference was noted in DO behavior, especially at the end of the reaction. It was observed that the rate at which the experimental DO raised, after the last minimum peak, was always stepper that the one predicted by the model. Also, substrate samples at the end of the reaction presented a value higher than the one predicted by the model. This lead to suspect that the degradation rate, and the DO uptake, was less than predicted by the model just after the maximum degradation rate was experienced. A way to explain this behavior is to modify the Haldane curve in such a way that it retains its characteristics for the inhibitory and the maximum biomass growth rate zone, but diminishes its activity suddenly below a certain threshold, near zero substrate concentration. Our proposed model to represents such a behavior is the modification of the Haldane law in Equation 3.

$$\mu = \begin{cases} \dfrac{\mu_0 S_C}{K_S + S_C + S_C{}^2 / K_I} & for \quad S_C \geq S_t \\ \mu_t S_C / S_t & for \quad S_C < S_t \end{cases} \qquad \text{Eq.(3)}$$

Where: μ_o, K_S, K_I, μ_t and S_t represent the maximum growth rate, the saturation constant, the inhibitory constant and the threshold constants (slope and limit) for the first piece of the piecewise μ function, respectively.

A problem encountered was that the typical representation of the nonlinear Haldane graph does not allow the K-parameters (μ_o, K_I, K_S) to be treated statistically, i.e. to directly extract their mean values and confidence intervals, as the results of mixing various experiments results do not correspond to averaging the μ graphs. A method for representing such same Haldane graphs, the S-parameters (μ^*,S^*,S_m) was used to avoid such a problem. Table 1 explains the physical meaning of the S-parameters. Equations 4 describe the parameter transformation.

Table 1 S-parameters definition and concept

S-Parameter names	Definition	Concept
μ^*	$\mu^* = \max(\mu(S))$	Maximum of the biomass growth rate. (S>0)
S*	$\mu(S^*) = \mu^*$	Substrate at which the maximum μ^* happens
Sm	$\mu(Sm) = \mu^*/2$	Substrate for medium (50%) inhibition. (for Sm>S*)

$$S^* = \sqrt{K_I K_S}$$
$$\mu^* = \frac{\mu_o}{1 + 2K_S / S^*} \qquad \text{Eq. (4)}$$
$$S_m = \frac{K_I + 4S^* + \sqrt{K_I^2 + 8K_I S^* + 12S^{*2}}}{2}$$

Once the two modifications to the model were implemented, the same process for identifying the parameters was followed and simulation results were compared to experimental data. Finally simulations were done to compare model predictions to real data using TOC strategy.

The fitting criteria for identifying the model parameters consisted of two parts. One includes the differences in substrate (modeled minus measured), the other the difference in DO. The final combined criterion weights both of them. Equation 5 describes such fitting criteria:

$$
\begin{aligned}
&Fc_k = Sc_k\textit{simulated}\text{-}Sc_k\textit{measured} && (k=1,\ldots,n;\quad n=\text{number of samples})\\
&Fo_k = So_k\textit{simulated}\text{-}So_k\textit{measured} && \text{Eq. (5)}\\
&F_k = W_o * Fo_k;\ F_{k+n} = W_s * Fc_k\\
&MQE = \mathrm{Sum}(F_i^2); && (i=1,\ldots,2n)
\end{aligned}
$$

Where: MQE, Fc_k, Fo_k, W_o, W_s are the Mean Quadratic Error, the fitting criterion for k^{th} substrate sample, the fitting criterion for the k^{th} DO sample and the DO and substrate weight coefficients, respectively.

Table 2 shows the Mean Quadratic Error (MQE) for the results obtained when identifying the parameters of both the individual experiments and the averaged model. It was observed, comparing the improved model with the classical one, an improvement of 66% for the averaged global MQE.

Table 2 Validation fitting results for the classical model and the improved model candidates

Model candidate	Experiment tag	MQE against individual identified own model	MQE against averaged Model	Averaged MQE	
				by group	Global
Classical	ID1	220	231	186	244
	ID2	127	141		
	VAL1		360	360	
Improved	ID3	12	42	51	81
	ID4	27	60		
	VAL2		141	141	

The sum of the quadratic values of the fitting criterion gives the MQE. For reference, if substrate concentration is assumed to be in the range [0, 200]mg/L and Oxygen concentration in the range [0, 10]mg/L, an error of *error %* (of maximum range) in all samples will yield a MQE as shown in Table 3. In practice not all samples do have the same error, so it must be kept in mind that errors contribute in a quadratic (not linear) way to the total error.

Table 3 MQE as function of error for ideal case of all errors being equal

error %	MQE
5	42
7	82
9	135
12	240
15	375

Figure 2 shows the result of a typical FTC batch experiment and compares it to simulations. The dotted line simulation does not include the DO sensor delay while the asterisked lines do. Circular marks represent offline measured data for substrate and distinguish the online measurements for DO. Note the better matching at the beginning and at the end of the reaction between experimental data and continuous line simulation when including sensor delay effects. This may not seem important for FTC operation, but is important if DO is to be used for TOC purposes.

Figure 3 shows the effect of including the Haldane modification in Eq. 3 to the model, for various S_t values. Note that at the end of the reaction the real substrate disappears at a slower rate than the simulated one if no Haldane discontinuity is used i.e. S_t=0. Such difference happens just after the system crosses the maximum biomass growth rate point. Increasing the S_t value allows to reproduce such phenomena.

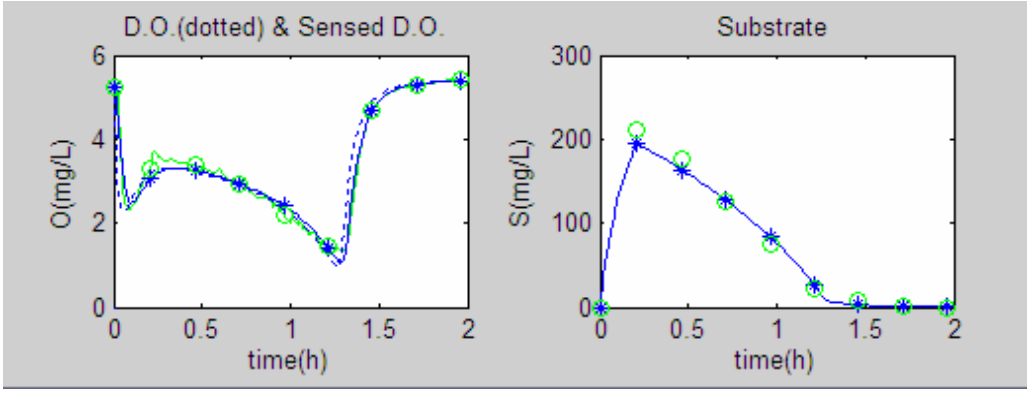

Figure 2 Experiment ID3 (FTC mode) model simulation comparisons. The dotted line represents the simulation of the classical model, without sensor delay effects. Note that dotted line is not visible in the substrate graph as it is the same as the continuous one (DO sensor has no effect on this variables)

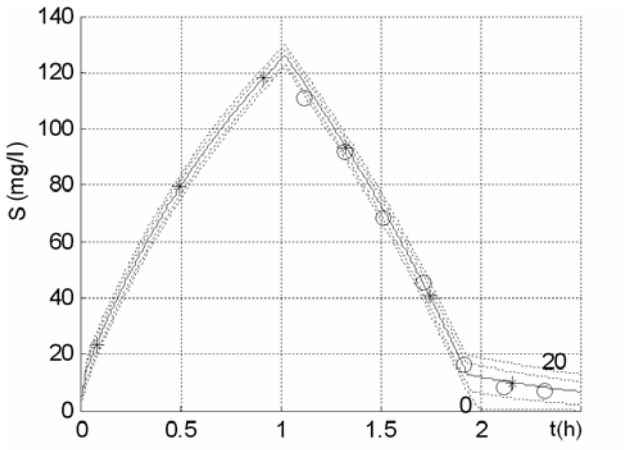

Figure 3 Effect in S-kinetics simulation (FTC mode) for different threshold values S_t=[0,7,13,17,20]

An implementation of the time optimal control strategy, called Event Driven Time Optimal Control (EDTOC) (Betancur *et al.* 2004), was used to conduct TOC experiments. A typical EDTOC kinetics is shown in Figure 4 along with simulations. The representation obtained with the improved model showed to be satisfactory for the control purposes.

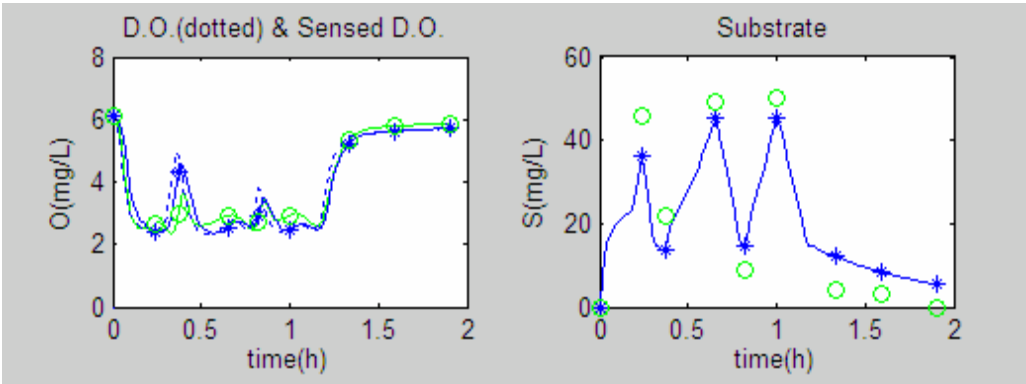

Figure 4 Experiment ID6 (TOC mode) versus model simulation comparison. Circular marks represent offline measured data for substrate and distinguish the online measurements for DO. The dotted line represents the simulation of the classical model, without sensor effect, but includes the Haldane piecewise modification. Lines with asterisk marks represent the model simulation when both sensor effects and Haldane modifications are added. Note that dotted line is not visible in Substrate (DO model does not affect substrate)

DO sensor model

An experiment was conducted by quickly moving the DO sensor from one beaker containing water without DO to another one with saturated DO conditions, once and again. Equation (2) was used to identify the time constants. Results are: τ_a=0.01h and τ_b=0.02h. Figure 5 shows the experiment results compared to the identified second order model simulation.

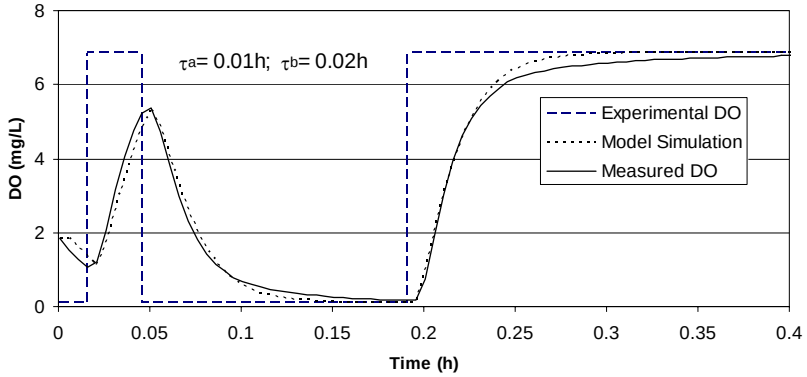

Figure 5 Experiment for identifying DO sensor. The dashed straight line is the real oxygen to which the probe was exposed (by quickly changing it from one beaker to another with opposite DO conditions). The continuous line is the sensed signal. The dotted one is the model simulation

Haldane parameters

Table 2 and Figure 6 show two different Haldane graphs and the averaging results. One of them is obtained by averaging the S-parameters, the other one by averaging the K-parameters. In this example it is clear that the mean of K-parameters is not related to the mean of the Haldane graphs. Using the S-parameters instead reduces the averaging error and gives results with logical physical meaning.

Table 2 Different Averaging methods of two Haldane graphs

Graph	S-parameters			K-parameters		
	μ^*	S^*	S_m	μ_0	K_I	K_S
Experiment 1	0.200	10.000	60.000	0.385	21.667	4.615
Experiment 2	0.140	18.000	72.000	1.260	4.500	72.000
S-Average	0.170	14.000	66.000	-	-	-
K-Average	-	-	-	0.822	13.083	38.308

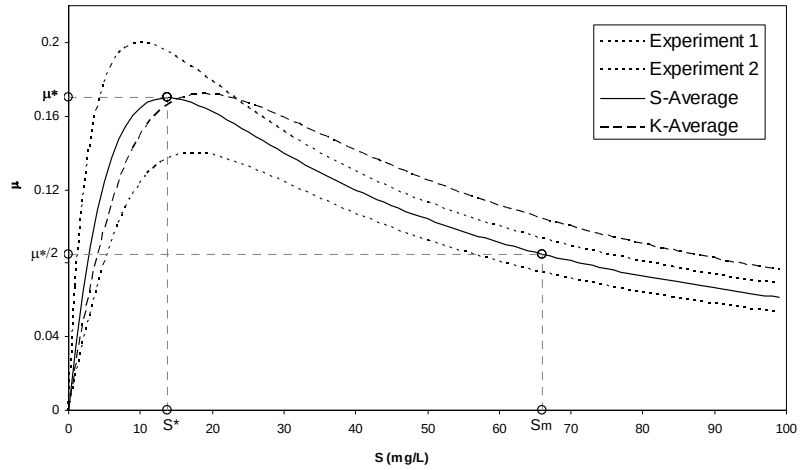

Figure 6 The dotted lines are two different Haldane identification results to be averaged. The continuous line is obtained by averaging each S-parameter (μ^*, S^*, S_m). The dashed one is obtained by averaging each traditional K-parameter (μ_0, K_I, K_S).

Conclusions

The fill and reaction phase model for the SBR in fed-batch mode was improved, without loosing simplicity, in such a way that the DO concentration behavior near the maximum biomass specific growth rate (μ^*) is better explained. This allows understanding and designing time optimal control strategies using DO as a control variable, instead of attempt using the, unavailable, substrate concentration measurement. In particular, the model was improved by including the DO sensor delay effects as a second order system, and the addition of a discontinuity in the Haldane model for the specific biomass growth rate.

S-parameters (μ^*, S*, and S_m) are introduced to represent the Haldane behavior. These allow an easy way to average the result of multiple experiments identification.

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The scientific responsibility rests with the authors.

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